

## **Update on the EPA/ORD Study on Emissions from Methyl bromide-treated Alfalfa**

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Three emission samples of each treated and untreated alfalfa (n=6) have been completed in the USEPA Open Burn Test Facility (OBTF) as described in the approved QAPP *Characterization of Emissions from Burning Methylbromide-Treated Biomass* (G-APPCD0030184). This represents 3-7 burns per sample, as multiple burns are necessary to get enough sample to detect trace pollutants.

The biomass was untreated alfalfa, from “Cal-Ranch” of Idaho Falls, a local commercial source, and treated alfalfa (ref. Robert Gourley email 6/8/2016).

Biomass was burned in the OBTF (Figures 1 and 2) at the in situ field density, 0.9 kg/m<sup>2</sup>.



Figure 1. Burn test in progress.



Figure 2. Typical post-burn appearance.

The as-received alfalfa (treated and untreated) was sent to ALS (Salt Lake City, UT) out for  $\text{Cl}^-$  and  $\text{Br}^-$  analyses. One set of raw biomass was sent out pre-November and the other in November, 2017. Residual ash after our burn tests was also analyzed. There was one burn with the raw biomass analyzed pre-November and two burns with the raw biomass analyzed in November. Results are summarized in Table 1.

Table 1. Raw Biomass and Ash Analysis

		$\text{Br}^-$ (ppm)	$\text{Cl}^-$ (ppm)	Date sampled
Treated Alfalfa	Raw Biomass	4780	2960	Pre-Nov
	Raw Biomass	2550	3380	Nov.
Untreated Alfalfa	Ash	8490	6430	Pre-Nov
	Ash	4950	4030	Nov.
	Ash	5220	3690	Nov.
	Raw Biomass	<21	6710	Pre-Nov
	Raw Biomass	<20	2030	Nov.
	Ash	428	13900	Pre-Nov
	Ash	<20	4490	Nov.
	Ash	<20	6760	Nov.

- Initial concentrations of  $\text{Br}^-$  ion average 3,600 ppm in the treated alfalfa.
- Both raw alfalfa types (MeBr-treated and untreated) exhibit high levels of  $\text{Cl}^-$  ion.
- The ash (which actually is a mixture of burned and unburned biomass) concentrates both the  $\text{Br}^-$  and  $\text{Cl}^-$  ions by about a factor of 2/1 (perhaps 3/1 if all of the raw biomass was consumed by fire).
- Concentrations are surprisingly variant for both  $\text{Br}^-$  and  $\text{Cl}^-$  ions, both in the raw biomass and the ash.

Alfalfa was hard to ignite and hard to sustain combustion. Most burns were relit at least once (using a propane torch). The untreated alfalfa had an ash weight of 19.3% whereas the treated alfalfa had a 29.0% ash weight.

$\text{PM}_{2.5}$  results (Figure 3) show that the treated biomass had lower average  $\text{PM}_{2.5}$  levels than the untreated biomass although considerable overlap is present. Over 97% of the PM mass is of mass median diameter  $1\ \mu\text{m}$  or less.

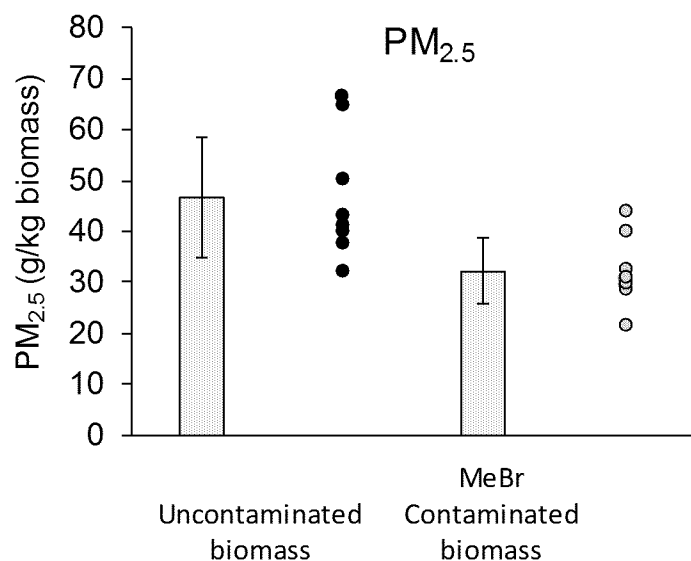


Figure 3. PM<sub>2.5</sub> results.

Br<sub>2</sub> and HBr were collected using NIOSH methods with coated filters. Both Br<sub>2</sub> and HBr were not detected (one sample each). The detection limit for HBr on the treated alfalfa was < 0.1 mg/m<sup>3</sup> (200 mg HBr/kg biomass) and on the untreated alfalfa was < 0.2 mg/m<sup>3</sup> (300 mg HBr/kg biomass). Difficulties were encountered with the Br<sub>2</sub> sample as the filters plugged quickly.

VOC results are shown in Table 2.

Table 2. VOC Emissions Results

VOC	Untreated			Treated		
	Average	std dev	RSD	Average	std dev	RSD
	mg/kg biomass	mg/kg biomass	%	mg/kg biomass	mg/kg biomass	%
Propene	2042	752	37	2253	166	7
Chloromethane	2147	866	40	1106	376	34
1,3-Butadiene	443	141	32	627	22	3
Bromomethane	2	1	43	739	207	28
Chloroethane	11	5	42	8	1	18
Ethanol	91	37	41	77	19	25
Acetonitrile	1906	700	37	2392	473	20
Acrolein	642	340	53	607	326	54
Acetone	2384	659	28	2123	388	18
Acrylonitrile	211	93	44	382	26	7
Vinyl Acetate	2063	636	31	1234	349	28

2-Butanone (MEK)	980	347	35	753	72	10
n-Hexane	59	30	51	51	12	24
Tetrahydrofuran (THF)	18	5	28	11	2	15
Benzene	507	122	24	820	37	5
n-Heptane	43	22	52	34	4	12
Toluene	1069	559	52	1077	99	9
2-Hexanone	28	11	40	22	2	11
Ethylbenzene	181	100	55	205	22	11
m,p-Xylenes	173	79	46	153	11	7
Styrene	233	129	56	296	20	7
o-Xylene	68	37	54	64	7	11
n-Nonane	25	15	60	18	3	16
Cumene	6	3	57	8	1	8
n-Propylbenzene	33	21	63	32	5	17
1,3,5-Trimethylbenzene	10	6	65	9	1	15
1,2,4-Trimethylbenzene	35	24	70	33	4	12
d-Limonene	24	6	25	20	8	39
Methyl Acetate	1422	599	42	1006	123	12
Thiophene	11	5	40	14	1	9
Indan	12	7	60	12	1	10
Indene	37	23	62	63	2	3

Brominated VOC results are shown in the Table 3. Bromomethane was the only detectable compound; it was most predominant with the treated biomass.

Table 3. Brominated VOC Emissions Results

VOC	Untreated mg/kg biomass	std dev	RSD %	MDL $\mu\text{g}/\text{m}^3$	Treated mg/kg biomass	std dev	RSD %	MDL $\mu\text{g}/\text{m}^3$
Bromomethane	2.3	1.0	43		739	207	28	
Bromodichloromethane	ND			1.4	ND			2.5
Dibromochloromethane	ND			1.5	ND			2.6
1,2-Dibromoethane	ND			1.5	ND			2.6
Bromoform	ND			1.4	ND			2.5
1,2-Dibromo-3- chloropropane	ND			0.92	ND			1.6
Vinyl Bromide	ND			2.0	ND			3.4
Dibromomethane	ND			1.9	ND			3.3
Bromobenzene	ND			2.3	ND			4.1

Carbonyl emissions (see Table 4) such as formaldehyde, acetaldehyde, and acetone were about 50% higher with the treated biomass than the untreated. Only single samples were

determined.

Table 4. Carbonyls Emissions

	Untreated	MDL	Treated	MDL
	g/kg biomass		g/kg biomass	
formaldehyde	134.8	0.014	169.7	0.02
acetaldehyde	319.4	0.056	552.3	0
acetone	143.1	0.079	240.5	0.08
propionaldehyde (w/acro product)	77.1	0.059	108.3	3
crotonaldehyde	20.8	0.078	32.5	0.11
butyraldehyde	83.7	0.066	109.4	0.09
benzaldehyde	37.4	0.11	46.4	4
isovaleraldehyde	26.7	0.13	40.4	0.16
valeraldehyde	ND	0.090	ND	0.19
o-tolualdehyde	ND	0.18	ND	0.13
m-tolualdehyde	ND	0.17	ND	0.26
p-tolualdehyde	ND	0.15	ND	0.24
hexaldehyde	ND	0.10	ND	0.22
2,5-Dimethylbenzaldehyde	ND	0.13	ND	0.15

The average PAH concentration from three trials of the contaminated and uncontaminated alfalfa is shown in Figure 4. ANOVA analyses ( $F = 14$ ,  $p = 0.0005$ ) showed that there was a significant difference in PAH emission between non Br-contaminated and Br-contaminated alfalfa with higher emissions from Br-contaminated alfalfa ( $160 \pm 8.6$  mg/kg biomass) than non Br-contaminated alfalfa ( $76.6 \pm 11.0$  mg/kg biomass). The most abundant PAH for both uncontaminated and contaminated was naphthalene comprising of approximately 68% of the total PAH emission factors. Acenaphthylene, phenanthrene and fluorine follow naphthalene in concentration.

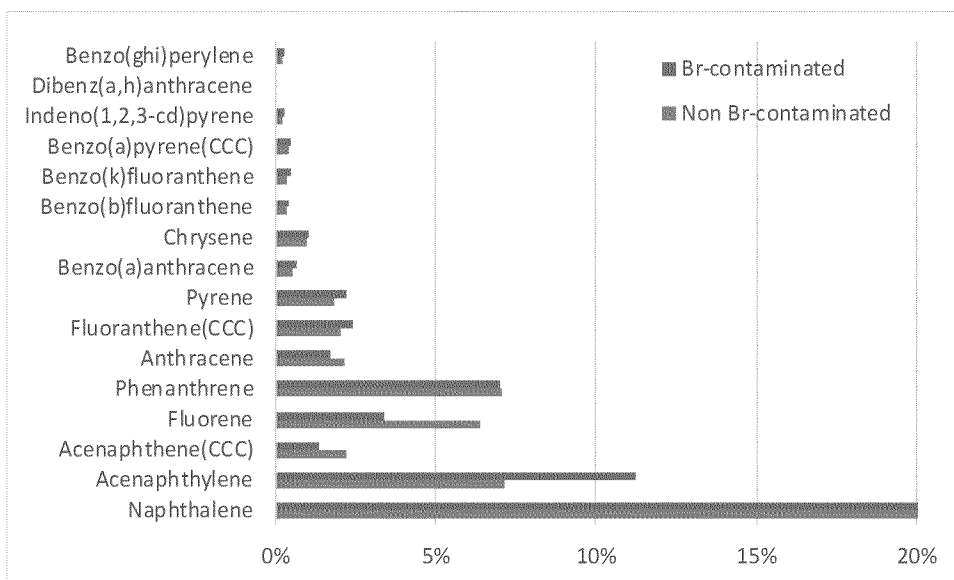


Figure 4. PAH Emissions from Contaminated and Non-contaminated Biomass

Three emission samples for each biomass type (total = 6) were gathered for brominated and chlorinated dioxins and furans. Analyses is only available for one of the sample pairs due to a problem with the HRMS (a service call has been placed). Preliminary results from the one sample pair show that the treated biomass has higher levels of chlorinated dioxins/furans (5.7 ng TEQ/kg alfalfa versus 0.58 ng TEQ/kg alfalfa) and brominated dioxins/furans (1.7 ng TEQ/kg alfalfa versus 0.4 ng TEQ/kg alfalfa, both with non-detects = 0). This is illustrated in Figures 5 and 6.

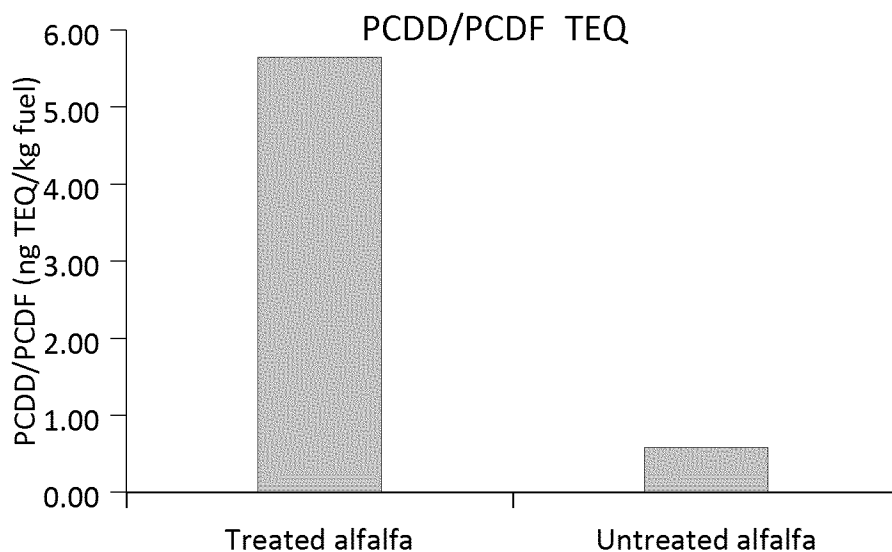


Figure 5. PCDD/PCDF Emissions

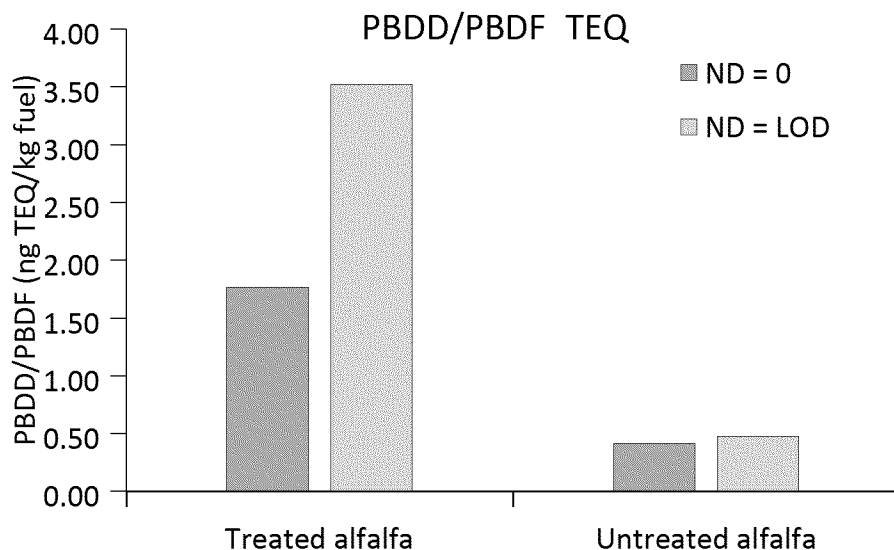


Figure 6. PBDD/PBDF Emissions

One test was conducted to simulate the effect of an air curtain incinerator (ACI). A blower was set to flow air over the alfalfa during combustion. Two control trials (no fan) and two test trials (blower fan) showed that the fan decreased the ash weight by 39% indicating better combustion. Subsequent tests with full emission sampling during ACI-simulated burns were not successful. Again, the biomass was very difficult to ignite. Initiating the air-assist blowers tended to blow the flames out, despite moving the fans back away from the fire. It appeared that the air-assist blowers enhanced propagation of the smoldering process. Difficulties in clearing the smoke out of the facility suggested the baghouse ID fan was operating poorly. The fan was adjusted and the belts tightened. A second day's attempt was made but it was determined that the smoldering combustion was producing so much sticky soot that the baghouse bags were sealing up. This was confirmed by a duct velocity measurement prior to burning (6.3 m/sec) followed by a measurement 5-10 minutes after burning (0.3 m/sec).

### Summary

For all but  $PM_{2.5}$ , measured emissions were lower for the untreated biomass. Since the treated and untreated biomass were from a different alfalfa source and may have different ages and moisture conditions resulting in different combustion behavior, this represents an imperfect comparison. The concentration of Br ion in the biomass ash doubled. Tests simulating an air curtain incinerator resulted in less ash (better burnout). Follow up tests to measure emissions under these conditions resulted in minimal flaming combustion and prolonged smoldering which blinded the baghouse with a tarry soot. These results suggest that if improved combustion can be accomplished in an air curtain incinerator, perhaps with a fuel assist burner and higher temperatures, better burnout could be achieved in comparison to an open field burn scenario. This approach would remove the bromide ion from the field, concentrate it in the ash for landfill disposal, and remove its potential for subsequent crop uptake.